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# An alternative to the JMAK equation for a better description of phase transformation kinetics

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**Abstract** The kinetics of phase transformations is usually described by the Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation. The article shows that this equation cannot give a sufficiently general description of austenitization kinetics of ferritic nodular cast iron. Therefore, another kinetics equation is proposed which catches the main circumstances and substance of austenitization more accurately than the JMAK equation does. It shows that the crucial phenomena in the transformation are not only the processes of the creation and growth of new austenite grains but also the change in specific volume and the chemical liquation of alloying additives, which retard the subsequent conversion. The proposed equation together with the Arrhenius equation allows describing simultaneously the temporal and temperature dependence of austenitization conversion including the partial transformation at insufficiently high overheating of transformed iron. It is verified by successful regression of experimental data, whose results allow drawing predictive curves for temperatures from the experimental temperature region or from its near vicinity, for which the conversion was not determined.

## Introduction

Nodular cast iron can be used for many industrial components such as gear wheels, valve levers of diesel engines, crankshafts, piston rods, etc. A considerable part of its production is applied in military industry, above all as components of military vehicles and some types of armour. For example, in 1995, United States used 3% of the whole production of nodular cast iron to this purpose [1] and this amount is increasing from year to year. Austenitization studied in this article is the starting point of heat treatments leading to increased strength of cast irons and steels, i.e. quenching and austempering.

The kinetics of austenitization [2–6] and of phase transformations in general is mostly described by the Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation [7–9]. Here it will be used in the form

$$p(t) = 1 - \exp(-k^n t^n) \tag{1}$$

where $p$ is the conversion, i.e. the relative content of the newly created phase. By theoretical considerations, the Avrami exponent $n$ acquires the integer or half-integer values in the range from 0.5 to 4, depending on the type and the conditions of the transformation under study. As the conditions during the transformation process substantially change with the conversion extent and temperature, the value of parameter $n$ can also change substantially in the range considered. However, in the regression of experimental data, mostly one value is considered for the whole transformation at the given temperature.

Advanced regression calculations of highly accurate measurements have shown mainly in last 10 years [10, 11] that using the JMAK equation for the description of phase transformations can sometimes lead to quite inaccurate or even invalid results. Therefore, different extensions and modifications of the JMAK model have been made [12–15]. One of them is the very promising equation by Starink [14]

$$p(t) = 1 - \left[\frac{(k\,t)^n}{\eta} + 1\right]^{-\eta} \tag{2}$$

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introducing the impingement parameter $\eta$, which seemed to be able to fit most of the deviations from the JMAK equation.

The temperature dependence of conversion variable $p$ usually consists in the temperature dependence of rate constant $k$ according to the Arrhenius equation. To simplify the regression calculations and to introduce only meaningful and practical regression parameters, the equation will be used in the form

$$k(T) = k(T_0)\exp\left[-\frac{\varepsilon}{\kappa}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{3}$$

where $\varepsilon$ is the activation energy of the transformation studied, $\kappa$ is the Boltzmann constant, and $T_0$ is a suitably chosen relative temperature. If this temperature is chosen from the range of test temperatures, the variation of regression parameter $k(T_0)$ is relatively low. The usual form of the Arrhenius equation (i.e. without fraction $1/T_0$ in Eq. 3) can be interpreted as Eq. 3 with infinite relative temperature. Then the standard deviation of the pre-exponential parameter $k(T_\infty)$ can be extremely high, sometimes even in orders higher than its average value.

The JMAK equation is mostly written in the form

$$p(t) = 1 - \exp(-k\,t^n) \tag{4}$$

If the Avrami exponent $n$ is not an integer or a simple fraction, the unit of rate constant $k$ corresponding to the form of Eq. 4, i.e. $s^{-n}$, is quite complicated and exotic. Therefore, the form of Eq. 1 is more suitable for practical use. If the JMAK equation is used in combination with the Arrhenius equation, the types of equations are not dependent on the choice between the JMAK equation forms (1) and (4). The difference consists only in the values of parameters $k(T_0)$ and $\varepsilon$. The value of pre-exponential parameter $k(T_0)$ is not a very important result from the viewpoint of materials engineering. On the other hand, the values of activation energy are quite significant characteristics of the transformation under study. The application of the forms (1) and (4) leads to different values of activation energies: the value $\varepsilon_{(4)}$ corresponding to the form (4) is equal to the product $n\varepsilon_{(1)}$, where the value $\varepsilon_{(1)}$ corresponds to the form (1).

The aim of the article is to describe the kinetics of austenitization of nodular cast iron (and evidently also of steels) using a sufficiently simple kinetics equation, which enables besides the regression of experimental results also the construction of predictive curves for unrealized temperatures from the range of the realized temperatures or from its close vicinity. As the JMAK equation can be used only to a limited extent, a new kinetics equation is proposed and verified, which enables a sufficiently general description of austenitization kinetics including the partial converse at insufficient overheating.

## Experimental

For the study of austenitization kinetics the experimental dependence of the content of transformed phase on time and temperature published in [16] was chosen. This article describes the austenitization of ferritic nodular cast iron in a temperature range from 800 to 1,050 °C, with a 50 °C step. The austenite content for each time and temperature was determined as an area portion of martensite, which transformed after quick cooling of austenite created up to a defined time. More details can be found in the original paper [16]. Experimental results are presented in Fig. 1 (see only the experimental points).

## Regression with the JMAK equation

To simplify the regression, let one individual value of the Avrami exponent be assumed for the conversion at a given temperature. Then the experimental values for each test temperature can be fitted using the JMAK Eq. 1 with the exception of a temperature of 800 °C, when full austenitization of ferrite was not reached. For this case it is necessary to multiply Eq. 1 by the parameter $a < 1$ (or $a < 100\%$), which means the maximum content of austenite at this temperature after a very long transformation time. With this parameter included in the regression, the value of $57.4 \pm 1.2\%$ is calculated. Considering the individual values of parameters $k$ and $n$ for each of the six temperatures, the regression with 13 parameters (two parameters $k$ and $n$ multiplied by 6 temperatures plus parameter $a$) leads to the fit presented in Fig. 1.

Each of the six curves in Fig. 1 fits the experimental points corresponding to the chosen temperature quite

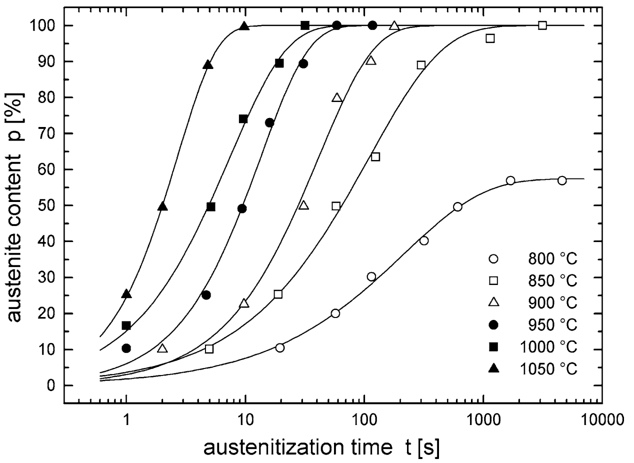

**Fig. 1** Relative content of newly formed austenite in dependence on temperature and austenitization time [16] (each temperature is fitted separately using the JMAK Eq. 1)

successfully, but on the other hand, the family of curves presents some irregularities. The distances between neighbouring curves and the slopes of curves at the points of inflection show no monotonous trend; moreover, the curves for 850 and 900 °C intersect, which is not theoretically possible in principle. The values of parameter *n* change in a relatively wide range from 0.6 to 1.3 and, when the temperature of 1,000 °C is not considered, the values monotonously increase with increasing temperature; see the second row in Table 1. The values of rate constant *k* increase monotonously with temperature from $4.7 \times 10^{-3}\ \mathrm{s}^{-1}$ for 800 °C to $3.8 \times 10^{-1}\ \mathrm{s}^{-1}$ for 1,050 °C.

Another fit of experimental results can be done if the individual values of parameters *k* and *n* are not considered separately for each temperature but their dependence on temperature is used. For the rate constant $k(T)$ the Arrhenius equation is naturally applied, for the Avrami parameter $n(T)$ linear dependence seems to be convenient, which follows from the second row in Table 1 containing its individual values. The resulting regression leads to somewhat different values of the exponent *n* (see the third row in Table 1) and eliminates the problems with the intersection of regression curves (cf. Fig. 2 with Fig. 1), but the partial transformation at 800 °C must be solved introducing the additional parameter as in the previous case (here its value is 61.7 ± 2.3%). Therefore, another kinetics equation was looked for, which together with the Arrhenius equation allows a common description of austenitization over the whole range of the temperatures studied, including the partial transformation at the lowest temperature, without the necessity to introduce any additional parameter.

## Derivation of new kinetics equation

During the austenitization of nodular cast iron (and also steel), ferrite transforms into austenite of a lower specific volume than the specific volume of ferrite. For this reason mechanical stress arises in the material being converted, which acts against the continuing transformation. On the other hand, the contribution of this effect is limited because of active creep at the transformation temperatures, which can decrease or nearly relax the internal stress mentioned. Another brake on the continuing transformation consists in chemical liquation: the low silicon content in austenite transformed in the initial stage leads to increasing silicon content in the later-transformed austenite, which makes the transformation more and more difficult. Generally speaking, the two mechanisms mentioned cause that the newly formed austenite decreases the rate of transformation of the ferrite that has not transformed yet.

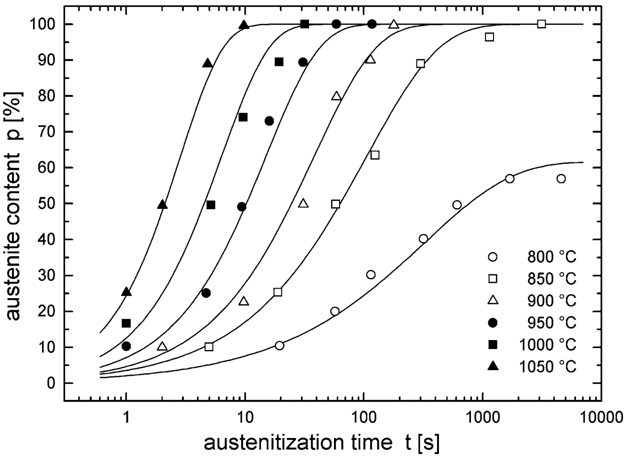

**Fig. 2** Relative content of newly formed austenite in dependence on temperature and austenitization time [16] (linear dependence of parameter *n* is considered together with the Arrhenius Eq. 3 for rate constant *k*)

In nearly every larger textbook of chemical kinetics the opposite effect called *autocatalysis* is studied: the product of reaction increases the rate of that reaction. The temporal dependence of conversion variable $x(t)$ during autocatalysis is described by the equation

$$x(t) = 1 - \frac{k_0 + k}{k_0 \exp[(k_0 + k)t] + k} \tag{5}$$

where $k_0$ is the rate constant of original non-catalyzed reaction, and *k* is a certain multiple of the rate constant of catalyzed reaction. Austenitization can then be approximately modelled by the equation of autocatalysis with the negative sign of parameter *k*, i.e.

$$p(t) = 1 - \frac{k_0 - k}{k_0 \exp[(k_0 - k)t] - k} \tag{6}$$

which can be called *autoinhibition* as an antonym of autocatalysis. The temperature dependence of parameters *k* and $k_0$ can be described by the Arrhenius Eq. 3 with different activation energies $\varepsilon$ and $\varepsilon_0$.

**Table 1** Dependence of the value of the Avrami exponent *n* on austenitization temperature

| Temperature (°C) | 800 | 850 | 900 | 950 | 1000 | 1050 |
|---|---|---|---|---|---|---|
| Exponent *n* (individual for each *T*) | 0.64 ± 0.04 | 0.70 ± 0.04 | 0.93 ± 0.09 | 1.07 ± 0.08 | 0.91 ± 0.06 | 1.29 ± 0.03 |
| Exponent *n* (linear function of *T*) | 0.59 ± 0.05 | 0.71 ± 0.04 | 0.84 ± 0.03 | 0.96 ± 0.04 | 1.09 ± 0.06 | 1.21 ± 0.08 |

## Regression using the new equation

The regression of experimental results [16] using the equation of autoinhibition (6) together with the Arrhenius Eq. 3 is presented in Fig. 3. The family of curves is determined by only four parameters $k(T_0)$, $k_0(T_0)$, $\varepsilon$, and $\varepsilon_0$ (the relative temperature $T_0$ is firmly given), therefore the fit can be considered very successful. However, the most important advantage of the new equation consists in the fact that the partial transformation need not be artificially implemented but it is a direct consequence of Eq. 6.

The very successful expression of the main trend of austenitization allows constructing the predictive curves for temperatures within and in close vicinity of the range of test temperatures (see Fig. 4). For temperatures from 740 to 820 °C a partial transformation is predicted directly by kinetics Eq. 6.

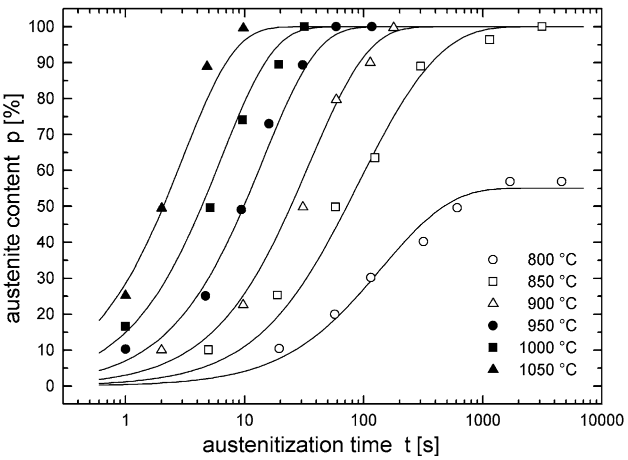

**Fig. 3** Relative content of newly formed austenite in dependence on temperature and austenitization time [16] fitted by the equation of autoinhibition (6) together with the Arrhenius Eq. 3

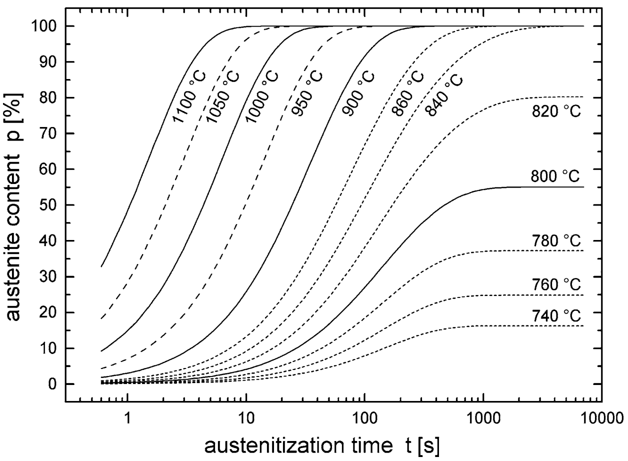

**Fig. 4** Family of predictive curves for the temperatures presented. Prediction is based on regression, using Eqs. 6 and 3 or 9, see Fig. 3

## Specific properties of the new equation

Figure 4 shows that at austenitization temperatures below 840 °C the transformation can proceed only partially. A limit temperature $T_\mathrm{m}$ must exist that separates the temperature ranges of total and partial transformations. The limit of Eq. 6 for very long times is

$$\begin{aligned} p(t \to \infty) &= 1 \quad &\text{for} \quad k_0(T) > k(T) \\ p(t \to \infty) &= \tfrac{k_0(T)}{k(T)} \quad &\text{for} \quad k_0(T) < k(T) \end{aligned} \tag{7}$$

Then for the limit temperature $T_\mathrm{m}$ given above, the equality $k_0(T_\mathrm{m}) = k(T_\mathrm{m})$ is valid, which leads to the equation

$$\frac{1}{T_\mathrm{m}} = \frac{1}{T_0} + \frac{\kappa}{\varepsilon_0 - \varepsilon} \ln \frac{k(T_0)}{k_0(T_0)} \tag{8}$$

determining explicitly this temperature. For the direct regression calculation of this temperature (not only its value but, above all, its standard deviation), it is suitable to substitute the regression parameters $k(T_0)$ and $k_0(T_0)$ by the parameters $T_\mathrm{m}$ and $K \equiv k_0(T_\mathrm{m}) \equiv k(T_\mathrm{m})$. Then the Arrhenius equation for the rate constants $k(T)$ and $k_0(T)$ has the form

$$\begin{aligned} k_0(T) &= K \exp\left[-\tfrac{\varepsilon_0}{\kappa}\left(\tfrac{1}{T} - \tfrac{1}{T_\mathrm{m}}\right)\right] \\ k(T) &= K \exp\left[-\tfrac{\varepsilon}{\kappa}\left(\tfrac{1}{T} - \tfrac{1}{T_\mathrm{m}}\right)\right] \end{aligned} \tag{9}$$

As a direct result of regression using the Arrhenius equation in the form of (9) the value of limit temperature is obtained, $T_\mathrm{m} = 832.1 \pm 7.6$ °C.

## Discussion

The equations of chemical kinetics are used for the description of chemical reactions but they can be also used for an approximate description or modelling of structural changes, which are of purely physical nature (usually based on diffusion). Besides the thermodegradation kinetics of polyamide composites [17], they were successfully applied to modelling the changes in hardness and resistivity of beryllium bronze during age-hardening [18] and for the description of dimensional changes of bearing steels during exposures at elevated temperatures [18, 19]. Then it is not surprising that austenitization, too, can be approximately described or modelled by this type of equation.

The changes in the structural and chemical composition of metals are substantially different in their nature but, nevertheless, they have some very general common features. The driving force behind both of them consists in the decrease of their total energy towards its minimum. Both changes are composed of single barrier processes when a barrier must be overcome by thermal activation. A general description of these processes can be made with high accuracy using the Arrhenius equation.

A simple description of austenitization kinetics cannot take all aspects of the transformation into consideration. Therefore only the most important aspect or aspects should be expressed and described. On the other hand, when the equation of autoinhibition describes austenitization better than the JMAK equation does, the counteraction of the newly formed phase against continuing conversion due to different specific volumes and due to chemical liquation of additive and alloying elements must play a more substantial or at least comparable role as the course of nucleation and growth of the new phase.

The necessity to choose either the JMAK equation describing the nucleation and growth of the new phase or the equation of autoinhibition describing the counteraction of the new phase led to the idea of combining both these principles. A differential equation describing this situation is not analytically solvable but it can be solved numerically, e.g. using the Runge–Kutta method directly during the regression calculations. This regression gave a very low value of the Arami exponent with high variation, $n = 0.04 \pm 0.05$. As equality $n = 0$ represents here the equation of autoinhibition alone, it can be said that the equation of autoinhibition in itself is fully sufficient for the description of the austenitization studied.

The classical derivation of the JMAK equation leads to integer or half-integer values of the Avrami exponent $n$. Table 1 shows that the calculated values of the exponent do not correspond to the theoretical values, and with some exceptions they are relatively far from them. Also, the monotonous increase of this exponent with temperature (with the exception of 1,000 °C) disagrees with the starting idea that a certain mechanism of transformation is connected with a certain value of the Avrami exponent.

Silicon used in graphitic cast irons as a graphitization additive causes that one constant eutectoid temperature in the basic Fe–C diagram changes into a temperature interval, whose position and width substantially depend on the silicon content. For the 2.64 wt% Si iron under study this range should cover the interval approximately from 775 to 840 °C [20]. The value of limit temperature $T_m = 832.1 \pm 7.6$ °C calculated using Eq. 6 and the family of predictive curves based on Eq. 6 are another indirect evidence that the kinetics equation of autoinhibition expresses the main feature of austenitization.

Regression calculations give substantially different values of activation energies: the higher value $\varepsilon_0 = 2.12 \pm 0.07$ eV $\equiv 205 \pm 6$ kJ/mol corresponds to proper austenitization, the lower value $\varepsilon \approx 0.22$ eV $\equiv$ 21 kJ/mol corresponds to retardation of the converse due to increasing silicon content in gradually created austenite and, to a limited extent, due to the mechanical stress which is the consequence of different specific volumes of the initial and the final phase. This means that the temperature dependence of austenitization rate is very strong while the rate of converse retardation is only weakly temperature-dependent. The weak temperature-dependence of retardation is connected with both mechanisms of retardation: (i) the temperature dependence of internal mechanical stress is comparable with the weak temperature dependence of the Young moduli in tension and compression of both phases present in transforming iron, (ii) diffusion of small silicon atoms in comparison with big iron atoms is very high in the whole interval of transformation temperatures considered and, therefore, the temperature change does not play too significant a role in silicon liquation.

No matter how successful the description of austenitization kinetics of ferritic nodular cast iron with using autoinhibition Eq. 6 is, it only expresses a very general statement: the newly created phase retards the transformation of the phase that has not transformed yet. Therefore it is more or less only a phenomenological or at most semi-phenomenological description and this limitation cannot be overcome without a much deeper study than the one presented in paper [16]. Substantial progress in mechanistic understanding of the transformation could be made on the basis of a very detailed microstructural analysis contrasted with modelling the temporal development of thermodynamics of the phase system studied or directly with modelling the diffusion processes during transformation. Another or complementary approach might consist in following the mechanical stress caused by different specific volumes of the original and the newly created phases and, in particular, its relaxation with respect to the transformation temperatures and temporal course of the transformation. Without this deeper study it is not possible to advance from a semi-phenomenological description to understanding the substance of the processes determining austenitization kinetics.

## Conclusions

On the basis of the results of regression and modelling of austenitization kinetics of nodular cast iron, the following conclusions can be drawn.

1. The JMAK equation, which is used for the kinetics description of phase transformations most often, can be used for a trouble-free description of austenitization only for each temperature separately. In the case of partial transformation an additional parameter has to be introduced.
2. The newly used kinetics equation for the description of austenitization kinetics was chosen with respect to the

consideration that the newly formed phase acts against the continuing conversion (in chemical kinetics this mechanism is analogous to autoinhibition). This counteraction is caused by the change in the specific volumes of the initial and the final phase and by the chemical liquation of alloying additions.
3. The kinetics equation of autoinhibition together with the Arrhenius equation describes the dependence of the conversion degree at austenitization on time and temperature very precisely, including partial conversion, although it contains only four parameters.
4. Besides austenitization some equations of chemical kinetics can be used for an approximate description of other structural changes in materials based on diffusion, although their nature is purely physical.

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## References

1. Keough JR (1995) Foundry Manage Technol 123(11):27
2. Nath SK, Ray S, Mathur VNS, Kapoor ML (1994) ISIJ Int 34:191
3. Zhang W, Elmer JW, Debroy T (2002) Mater Sci Eng A 333:320
4. Elmer JW, Palmer TA, Zhang W, Wood B, Debroy T (2003) Acta Mater 51:3333
5. Elmer JW, Palmer TA, Babu SS, Zhang W, Debroy T (2004) Weld J 83:224S
6. Kumar A, Mishra S, Elmer JW, Debroy T (2005) Metal Mater Trans A 36:15
7. Johnson WA, Mehl RF (1939) Trans AIME 135:416
8. Avrami M (1939) J Chem Phys 7:1103
9. Kolmogorov AN (1937) Izv Akad Nauk SSSR, Ser Matem 3:355
10. Todinov MT (2000) Acta Mater 48:4217
11. Levine LE, Narayan KL, Kelton KF (1997) J Mater Res 12:124
12. Starink MJ, Zahra AM (1998) Philos Mag A 77:187
13. Schmidt U, Schmidt B (2000) Mater Sci Forum 331–333:889
14. Starink MJ (2001) J Mater Sci 36:4433
15. Starink MJ (2004) Int Mater Rev 49:191
16. Herfurth K, Giesserei-Praxis (2003) 99
17. Kohout J (1999) J Mater Sci 34:843
18. Kohout J (2004) J Phys IV 120:191
19. Kohout J (2007) Mater Sci Eng A 462:159
20. Dorazil E (1991) High strength austempered ductile cast iron. Horwood, London